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POSITIVE ION REACTIONS

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I. Introduction

Five years ago at the symposium preceding the present one, two reports summarized experimental work on collisions between ions and neutral atomic systems of interest to aeronomy.

J. F. Paulson (1) reviewed the situation with regard to experiments at thermal and low energies and the present author summarized experiments where the relative energy was sufficiently high that ion beam methods were employed (2). At that time the higher energy techniques were well established and a number of results had been obtained; however, to apply the results to problems of low energies extrapolation by rather unreliable means had to be employed. In only a few cases were thermal and low energy data available since the techniques of experimenting at these low energies were in a very early stage of development.

The five years intervening between these symposia has seen the situation reverse itself. The development of low energy experimental methods has been rapid and the amount of low energy data on the principal atmospheric species is now quite large. To an ever-increasing extent the role of the higher energy experiments is to examine details of reactions in order to better interpret the lower energy results as they apply to the atmosphere and to discover processes deserving of attention in thermal energy experiments.

Accordingly it is appropriate here to review the principal

laboratory methods now in use to obtain thermal energy data on total cross sections and reaction rate coefficients for ion-neutral reactions, to examine briefly the modifications of these methods and alternative methods by which the effects of increased kinetic energy and reactants being in excited states are assessed and to discuss the ways in which higher energy experiments contribute additional knowledge.

In the interests of brevity the entire field of very high energy (i.e., 1 kev and up) processes will be omitted in this review despite their importance to certain atmospheric phenomena. Only reactions involving positive ions will be considered here, since negative ion reactions are being treated in a separate review by E. E. Ferguson (3). Only casual treatment of methods which were described in the reviews (1 and 2) of the 1963 symposium will be made here, the reader being referred to these earlier papers; emphasis will be placed instead on some of the more important newer developments. Lastly, no attempt will be made to present a complete compendium of reaction rate coefficient results; instead a summary of only those reaction rate coefficients most commonly used in chemical aeronomy at low energies is given.

II. Information Needs and Capabilities

The large bulk of information of present interest to aeronomy is

limited to very low kinetic energies, i.e., in the energy range from about 0.015 ev to about 0.15 ev, for this is the range of temperatures in the ambient natural atmospheres of the earth and neighboring planets. While attention has been focussed initially on those atmospheric species which are the major constituents in the atmospheres, i.e., N_2 , O_2 and O , it has become increasingly evident that major aeronomic effects involving ions arise through minor atmospheric components such as O_3 , NO , OH , CO_2 , He and H . Additionally, mass spectrometric sampling of the D-region by Narcisi and his collaborators (4) has dramatically introduced an interest in reactions involving metals and other materials presumably of meteoritic origin.

While the catalogue of chemical species of interest has increased, the need for detailed information about the role of excited states of reactants has also become apparent. In several instances it has been found in the laboratory that cross sections and rate coefficients depend very strongly on the internal energy of one or both reactants. The importance of excited states in the normal atmosphere has not been well assessed as yet, but in rather special circumstances of a disturbed atmosphere, the effects of internal energy of reactants appear exceedingly important.

In general the information sought for low energy aeronomy is total cross section or reaction rate coefficient data and most experiments are directed at obtaining this type of information. The processes of interest that involve positive ions are (a) charge

transfer, e.g., $A^+ + BC \rightarrow A + BC^+$, and (b) ion-molecule reactions (or ion-atom interchange), e.g., $A^+ + BC \rightarrow AB^+ + C$, the distinction between the two being whether the chemical identity of the reactants is preserved or altered in the collision. While these names are good on laboratory experimental grounds, since the ionic products can be unequivocally determined by using mass spectrometry, the distinction physically is less clear. While charge transfer, for example, can proceed by simple electron transfer as in the case at high energies, low energy charge transfer products can also be formed in one of the decay channels of a transitory complex ion, $(ABC^+)^*$. Since ion-molecule reactions are normally envisaged as proceeding through such a complex ion, some and probably most thermal energy charge transfer reactions are more nearly similar to ion-molecule reactions than to simple electron transfer processes.

In simple electron transfer between systems of the same ionization potential (resonant charge transfer) the energy dependence of the total cross section is given by

$$[1] \quad Q = (A - B \log E)^2$$

where A and B are constants. When the process is endothermic this dependence is found at high energies but as the energy is reduced the cross section reaches a maximum at a relative velocity $v_m \approx a|\Delta E|/\hbar$ where ΔE is the energy defect and a is a length of atomic dimensions. At lower energies the cross section diminishes to zero at threshold

energy in the center of mass coordinates (see for example Ref. 5).

For exothermic processes the simple electron transfer cross section is expected to behave similarly, to the endothermic case, where ΔE is now the excess energy in the process. However, in cases involving molecules or molecular ions the products can be left in excited states thus leaving ΔE effectively zero. In such cases of "accidental resonance" charge transfer, Eq. [1] again describes the dependence of the cross section on energy.

The usual model taken for ion-molecule reaction collisions is that a collision complex is formed, and redistribution of the atoms within this complex occurs. In the case of ion-molecule reactions the mechanism of complex formation is that an incoming ion induces an electric dipole moment in a neutral, and the charge-induced-dipole force attracts the two together. If the initial impact parameter is above a critical amount depending on the relative velocity, the ion will be deflected slightly but probably no reaction will occur; if smaller than this critical amount, the two particles orbit around each other and come closer to where reaction can occur. The cross section for forming an orbiting complex was given by Langevin as

$$[2] \quad Q(v) = 2 e \sqrt{\frac{\alpha}{\mu}} \cdot \frac{1}{v}$$

where α is the polarizability of the neutral and μ the reduced mass.

Gioumousis and Stevenson (6) and Field, Franklin and Lampe (7) have established experimentally that for many ion-molecule reactions Eq. [2] does describe the cross sections at energies of a few eV and less. In some cases the inverse velocity dependence is observed but the absolute magnitude of a cross section is less than that predicted. In these cases, one recognizes that a collision complex can decay through various channels leading to new ionic products, to charge transfer and also to no change in products (i.e., scattering), and that the probability of decaying by any one channel will determine the cross section for that one process.

It is of interest to note that for processes described by Eq. [2], the rate coefficient,

$$[3] \quad k = \int Q(v) v f(v) dv$$

where $f(v)$ is the normalized velocity distribution function, is independent of any other parameters that might appear in $f(v)$; most notably it is independent of the temperature in the case of a Maxwell-Boltzmann distribution.

The two energy dependences given in Eqs. [1] and [2] are often used in extrapolation of high energy data to thermal energies, when it can be established that one or the other is valid at higher energies, and this procedure has usually given fairly good estimates of rate coefficients which have later been determined at very low energies.

In some cases it appears that charge transfer can proceed by both simple electron transfer and by complex formation, as evidenced by velocity dependences given by Eq. [1] at higher energies and by Eq. [2] at moderate energies. In some cases, most notably the important reaction $O^+ + N_2 \rightarrow NO^+ + N$, neither Eq. [1] nor Eq. [2] even crudely describes the experimental results.

It has already been pointed out that where a charge transfer process is exothermic it can still display an energy dependence corresponding to one of resonance charge transfer, i.e., Eq. [1]. This is usually taken to imply that the excess energy has been left as internal excitation in the products. Of course the possibility that a product of an ion-molecule reaction is left in an internally excited state is also present. Such products can radiate or dissociate, or, if metastable, remain to participate in future reactions. The last possibility is one of the reasons for studying the role of internal energy in aeronomic reactions even in the ambient atmosphere and the first two possibilities provide additional laboratory methods of studying reactions.

At higher energies, other two-body collisions processes occur. These include direct excitation and/or dissociation of either of the reactants, ionization of the target neutral, and removal of additional electrons from the incident ion, in addition to charge transfer. In general the formation of collision complexes is a low energy phenomenon and Eq. [2] fails at ion energies of the order of tens of ev, with

the cross section for ion-molecule reactions falling off much more rapidly as the energy is increased.

The principal three-body thermal energy process of interest to aeronomy is clustering, i.e., the addition of neutral molecules to existing ions. The case of clustering of one or more water molecules to ions is particularly noteworthy in the D-region.

III. Laboratory Methods

The laboratory methods in use for the measurement of total cross sections and reaction rates for processes involving positive ions and neutrals can be grouped on the basis of the energy range in which they work. The principal general methods are

1. Thermal energy methods. (0.008 - 0.05 ev)
 - a. Mass Spectrometry of Stationary Afterglows
 - b. Mass Spectrometry of Flowing Afterglows
 - c. Ion Cyclotron Resonance Methods
2. Thermal to medium energies. (0.025 - 10 ev)
 - a. Secondary Ions in Mass Spectrometer Sources
 - b. Pulsed Sources on Mass Spectrometers
 - c. Drift Tube Methods
 - d. Merging Beam Methods

3. Medium to high energies.

- a. Beams into Static Gases, Double Mass Spectrometer Methods
- b. Crossed Beam Methods

Most of these methods were described in the reviews given at this symposium five years ago (1 and 2), and these will not be discussed to any extent in the present summary except to note certain innovations to these older techniques and new results of unusual interest. Three of the methods are new, however, and these will be discussed in some detail. The three new methods are flowing afterglows (1b), ion cyclotron resonance (1c) and merging beams (2d).

1. Thermal Energy Methods.

a. Mass Spectrometry of Stationary Afterglows, Mass spectrometry of stationary afterglows was used several years ago to provide the earliest information on charge transfer and ion-molecule reactions of major importance to aeronomy. In this method a mixture of gases in widely disparate amounts are subjected to a pulse of excitation that produces primary ions from the original gases in amounts roughly proportional to their respective number densities. After cessation of the pulse, these primary ions react with the neutrals and the relative populations of the ions change in time. An aperture is placed in the afterglow chamber and ions emerging from the aperture are analyzed by a mass spectrometer. The assumption

is made that the ion currents are proportional to the number densities of the ions in the vicinity of the aperture and the time history of each ion is taken to represent the time history of the number density of each ion, from which a rate coefficient may be deduced if one also knows the partial pressures of the neutrals in the afterglow chamber. Such experiments were performed by Sayers and his associates (8 and 11), Hasted and his collaborators (9) and by Fite et al (10), and are described in Ref. 1.

In the past five years, the principal work done with stationary afterglows has been to take advantage of the small volumes involved which makes rather easy the variation of temperature and the study of temperature dependences of ion-neutral reaction processes. Sayers and Smith (11) studied the temperature dependence of $O^+ + O_2 \rightarrow O + O_2^+$, finding a rate that diminished with temperature which has subsequently been determined by Smith and Fouracre (12) to vary as $T^{-0.48(\pm 0.05)}$ up to about 600°K, in opposition to temperature independence expected on the basis of Langevin collisions. This result is in good agreement with a stationary afterglow experiment result of Nakshbandi and Hasted (13) and a flowing afterglow experiment of Dunkin et al (14). At temperatures higher than 600°K the rate coefficients as determined in a drift tube experiment of Bohme et al (15) and a secondary ion mass spectrometer experiment of Warneck (16) appear to be effectively temperature-independent up to several thousand degrees, i.e., in accord with the orbiting collision model (Eqs. [2] and [3]) and then

appear to increase with energy (15).

The fact that more has not been done with stationary afterglow mass spectrometry is due to two basic limitations of the general method. First the gases admitted to the afterglow chamber must be chemically stable and second, all gases are subjected to the excitation pulse. Since the excitation pulse can partially dissociate and excite a neutral gas, one is rarely completely certain that an observed reaction process is occurring with a groundstate molecule of the neutral gas put into the chamber nor certain of the state of the ion. One must work very hard to ensure an unambiguous interpretation of an experimental result.

These two basic problems have been largely alleviated in the flowing afterglow approach.

b. Mass Spectrometry of Flowing Afterglows. In the flowing afterglow technique which was developed and very successfully used by E. E. Ferguson, F. C. Fehsenfeld and A. L. Schmeltekopf and their collaborators (17) at the Environmental Sciences Services Administration laboratories in Boulder, Colorado, the variation of ion concentrations with time of the stationary afterglow approach is replaced by variation of ion concentrations with space as an afterglow flows rapidly down a tube. While this in itself offers no advantages, the method does represent a major step forward in that it permits injection of gases into the flow stream without their being subjected to the excitation mechanism making the primary ions and all that this implies.

In a typical experiment a buffer gas (usually helium) is admitted to the entrance end of the flow tube and subjected to electron impact bombardment or microwave power or some other means of producing ions. Slightly downstream, a primary gas is injected into the stream and charge transfer and Penning ionization operate to replace the helium ions by primary ions from the injected gas. Yet further downstream, a secondary gas is injected whose reactions with the primary ions are to be studied. Finally at the end of the flow tube the ions present are sampled by being taken into a differentially pumped mass spectrometer through an aperture normally on the axis of the flow tube. Typical flow speeds are 10^4 cm/sec, tube lengths are normally about 1 meter and the gas pressure (being made up almost entirely of buffer gas partial pressure) range are generally between 0.1 and 1 torr. The quantity of buffer gas handled is quite large and fast Roots pumps are used to maintain the flow and to exhaust the gas after the flow has passed the mass spectrometric sampling device.

As noted above, the advantage of this approach is that secondary gases are injected into the stream below the point where buffer gas ions and primary ions are made, thereby obviating questions of the uncontrolled production of excited states of the neutral reactants, questions which plague stationary afterglow experiments. Additional major advantages are that (1) the neutral gases need not be chemically stable but can be either partially dissociated, or put into some excited

state, in some specific and separately controlled manner, (2) the spatial separations admit optical absorption spectroscopic monitoring of species and states at any point in the flow, (3) additional gases can be injected which quench out states and species of primary ions whose presence would confuse interpretation of an experiment, and (4) different methods of injection and points of injection can be used to maximize or minimize either wanted or unwanted effects. The excitation means is usually run continuously, but the pulsed mode of excitation can also be employed to advantage. The flexibility afforded by being able separately to control so many of the parameters in flowing afterglow experiments is enormously greater than that available in stationary afterglow experiments, and the flowing afterglow method has now become the standard way of studying thermal ion-neutral reactions.

It would be misleading to suggest that the interpretation of flowing afterglow experiments is not without its problems. Some of these problems originate from the use of a flow system, and it is appropriate to consider the model of what takes place in the flowing afterglow. The flux of primary ions, S_1 , is presumed to be given by

$$[4] \quad S_1 = D_1 \nabla N_1 + N_1 v$$

where N_1 is the primary ion number density, D_1 is the ambipolar diffusion coefficient of the primary ions through the buffer gas

and v is the vector velocity of the stream which is determined by the hydrodynamics of the flow. Applying continuity in the steady state one can write down

$$[5] \quad \vec{v} \cdot \vec{S}_1 = -kn_1n_2 - \sum_{i \neq 2} \beta_{ii} n_i N_1 - \alpha_1 n_e N_1 + \gamma_1 n_1$$

where the first term represents the loss of primary ions due to the reaction of interest with a neutral gas whose number density is n_2 , the second term represents loss of primary ions due to other competing processes, the third term is the loss due to electron-ion recombination (and a similar term could be written down for ion-ion mutual neutralization) and the fourth term represents the production of primary ions by Penning ionization by He^* and other processes.

Combining these equations

$$[6] \quad (\vec{v} \cdot \vec{v}) N_1 = -kn_2 N_1 - \sum_i \beta_{ii} n_i N_1 - \alpha_1 n_e N_1 + \gamma n_1 + D_1 \nabla^2 N_1$$

The corresponding equation for a secondary ion formed as a product of the reaction between N_1 and n_2 is

$$[7] \quad (\vec{v} \cdot \vec{v}) N_2 = +kn_2 N_1 - \sum_j \delta_{jj} n_j N_2 - \alpha_2 n_e N_2 + \sum_j \epsilon_{jj} n_j N_j + D_2 \nabla^2 N_2 + \gamma_2 n_2$$

where the first term represents the process of interest, the second term losses of secondary ions in tertiary processes, the third term again recombination, the fourth term production of secondary ions in

reactions with ions other than the desired primary, the fifth term the ambipolar diffusion losses, and the sixth term production of ions by Penning ionization, etc.

The number density of the secondary gas(es) are themselves solutions of diffusion equations of the type

$$[8] \quad (\vec{v} \cdot \nabla)n_2 = D_n \nabla^2 n_2$$

subject to the boundary conditions and whatever initial conditions are appropriate to the chosen manner of injection.

The complexity of using these three equations and treating them properly is staggering. However, one can manipulate the experimental conditions to simplify the problem somewhat by minimizing the contributions of separate terms. For example, by using sufficiently low plasma densities the recombination terms can be neglected; Penning ionization by He^* as an unwanted source of primary or secondary ions can be excluded by admixing a small amount of Argon to the Helium buffer gas to quench the He^* ; using clean gases and controlling the means of production of chemically unstable neutral reactant species can minimize competing processes terms, etc. Indeed, much of the success of the ESSA group in using these experiments is due to their ingenuity in finding ways to manipulate gases and experimental parameters in order to display the process of interest.

There are additional problems however. Questions of mixing of

an injected reactant gas with the flow stream enter and are important especially at the high flow velocities used; the form of \vec{v} is important and although indications are that laminar viscous (Poiseuille) flow is operative over most of the length of most flow tubes, one does not know \vec{v} in the vicinity of obstructions such as nozzles where the reactant gases are injected. The fact that a pressure gradient along the tube is necessary to maintain the flow further complicates matters.

However, even under "ideal circumstances", i.e., no competing processes and Poiseuille flow, the situation is still not easy. In the cylindrically symmetric case, the equations become

$$[6'] \quad D_1 \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial N_1}{\partial r} \right) + D_1 \frac{\partial^2 N_1}{\partial z^2} = v_o \left(1 - \frac{r^2}{a^2} \right) \frac{\partial N_1}{\partial z} + kn_2 N_1$$

$$[7'] \quad D_2 \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial N_2}{\partial r} \right) + D_2 \frac{\partial^2 N_2}{\partial z^2} = v_o \left(1 - \frac{r^2}{a^2} \right) \frac{\partial N_2}{\partial z} - kn_2 N_1$$

$$[8'] \quad D_n \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial n_2}{\partial r} \right) + D_n \frac{\partial^2 n_2}{\partial z^2} = v_o \left(1 - \frac{r^2}{a^2} \right) \frac{\partial n_2}{\partial z}$$

where each D is a function of position due to the pressure gradient down the tube.

It is apparent that these three equations cannot be solved by separation of the variables due to the parabolic flow profile, and further approximations must be introduced. One of the simplest

approximations assumes that n_2 is constant (i.e., the neutral reactant is distributed uniformly), that N_1 is initially a function of z only and independent of the radius r , and that the flow is "slug flow", i.e., that $v = v_0$ and is independent of r . Under these extreme simplifying assumptions, $N_1(z)$ is given by

$$[9] \quad N_1(z, n_2) = N_1(0)f(r) \exp\left[-\left(\frac{D_1}{\Lambda^2} + kn_2\right) \frac{z}{v_0}\right]$$

after sufficient time (distance) has elapsed for the flow to settle into the lowest radial diffusion mode, for which the diffusion length is Λ , and where f is a Bessel function. Clearly, by varying n_2 and plotting N_1 on a semi-log plot, the slope gives an indication of the rate coefficient, k . This method of observing primary ion decay, after approximate corrections for parabolic flow is that normally employed by the ESSA group and has the advantage that by holding the geometry constant and spatial parameters in Eq. [9] are unchanged which also has the experimental advantage of making unnecessary the moving of sources of either the primary ions or the secondary gases.

It is to be pointed out, however, that if the ambipolar diffusion coefficient is dependent on n_2 this procedure can lead to erroneous results. Since ambipolar diffusion coefficients do change with relative concentrations in an ion mixture and since the ion concentrations are dependent on n_2 through the reaction, it would be expected that the ambipolar diffusion coefficient would be dependent on n_2 .

An alternative procedure in data treatment can be used to minimize macroscopic effects of this kind (and also competing process effects). If one defines a ratio, $R = N_2/N_1$, Eqs. [6'] and [7'] can be combined to give

$$[10] \quad (v \cdot \nabla)R = kn_2(1 + R) + R \left\{ D_2 \frac{v^2_{N_2}}{N_2} - D_1 \frac{v^2_{N_1}}{N_1} \right\}$$

which in the limit of small R gives

$$[11] \quad v \frac{\partial R}{\partial z} = kn_2(1 + R)$$

and which can be solved along the z -axis to give

$$[12] \quad \log(1 + R) = \frac{k}{v_0} \int n_2(0, E) dz$$

In this approach, even if n_2 is not uniform, solution of Eq. [8] is all that is needed in order to perform the integral.

This "ratio method" which was used by Farragher et al (18) in studying charge transfer between atmospheric ions and sodium atoms, has the disadvantage that one must know the detection efficiency for the primary and secondary ions. If there is mass discrimination in the mass spectrometer or differences in secondary emission coefficient at the electron multiplier detector, these must be corrected for before correct answers can be hoped for.

A third method for analyzing data is to treat the appearance of

the secondary ions. Like the decay of the primary ion method, it observes a single ion and therefore is not susceptible to mass discrimination effects. This method handles Eq. [7'] in a manner analogous to that used for Eq. [6'] in deriving Eq. [9]. In an analogous manner, problems of changing diffusion coefficients and other macroscopic effects that depend on n_2 can again lead to erroneous results.

The complexity of properly treating the physics in flowing afterglows is evident from the above discussion. There are, of course, other problems which are shared with stationary afterglow methods which have not received detailed consideration as yet. In particular the processes by which ions emerge through apertures is not at all well understood. The practice of biasing an ion extraction aperture which is often done to improve signal strengths suggests that the ion extraction process is mobility limited. There is some evidence suggesting that the existence of negative ions in the plasma affects positive ion extraction (19) and varying an added electronegative reactant gas may lead to spurious results using the primary ion decay method. There is a free jet expansion as the gas leaves the flow tube and enters the mass spectrometer's high vacuum; the extent to which altering gases affects this expansion and in turn the ion extraction has not been investigated.

In general, it seems appropriate to caution any user of rate coefficients obtained from flowing afterglow experiments that errors

of a factor of two or three may still be in even the best measurements. The physics of afterglows is quite complex and of flowing afterglows even more so. Factors of two discrepancies are not uncommon with ostensibly identical flow tubes and data handling procedures, even for the simplest processes having the largest rate coefficients. Time and further work on this very fruitful approach will unquestionably clear up some of these remaining problems.

To turn to the positive aspects of flowing afterglow experiments perhaps the best testament to the fruitfulness of the approach is the list of reactions at the end of this paper whose rate coefficients have been obtained by no other method. Two experiments are appropriate to recount here in the text as well. The first studied reactions of $N_2^+ + O$. (20) In this study nitrogen gas that had been partially dissociated in a separate discharge flowed through a side tube toward the flowing afterglow containing N_2^+ ions. Before admission to the flow, NO was added in the side tube and the titration reaction $NO + N \rightarrow N_2 + O$ produced oxygen atoms at the rate of one O for each NO added. Since the flow rate of NO could be measured, the flow of O into the afterglow was known and the experiment could proceed in a fairly conventional way.

The second particularly interesting experiment involved the reaction $O^+ + N_2 \rightarrow NO^+ + N$, thermal energy values of which had been particularly elusive and irreproducible from one investigator to another using stationary and flowing afterglows. The problem was

traced down in the experiment of Schmeltekopf et al (21) who excited the nitrogen in a separate gas discharge before admission to the flow tube. The excited neutral gas was then electron-impact excited to radiating states and from the vibrational temperature of the emitted radiation the vibrational temperature of the original excited N_2 gas was deduced. The remarkable finding was that as the vibrational temperature was increased the rate coefficient was increased enormously. Evidently the scatter in data from other experiments on this reaction arose from different experiments having nitrogen whose vibrational states were populated differently and the lowest value was the best. This $O^+ + N_2$ reaction has the strongest dependence on the internal energy state of the neutral reactant known so far. The fact that the process is also of unusual importance to aeronomy emphasizes the importance of excited states in understanding the upper atmosphere.

c. Ion Cyclotron Resonance Methods. Many of the uncertainties in the afterglow methods discussed above arise from lack of understanding of how ions emerge through apertures. Clearly these problems could be avoided if the rates of change of ion population could be determined while the ions were in the flow tube. A very attractive method by which this can be done is the use of ion cyclotron resonance.

In this method a magnetic field is put on the afterglow so that each ion follows a circular motion at the ion cyclotron resonance frequency,

[13]

$$f_c = \frac{1}{2\pi} \frac{eB}{mc}$$

where B is the magnetic induction, e is the charge, c is the velocity of light, and m is the ion mass. Obviously ions of different e/m will have different cyclotron energies. If a weak radio frequency electric field at the cyclotron frequency is also applied, an ion will pick up energy from the field and this energy absorption can be detected as a load on the rf oscillator. By sweeping either the magnetic field or the oscillator frequency, the appearance of loading on a marginal oscillator evidences the presence of each ion and the strength of the loading gives an indication of the number of ions present. By following the rise and decay rate of various ions one has the information from which reaction rate coefficients can be deduced.

This very attractive approach was first employed to study mobilities and total collision cross sections of ions by Wobschall, Graham and Malone (22), where the cross section information could be deduced from line widths of the resonance absorption lines. More recently it has been applied to charge transfer and ion-molecule reactions by Baldeschweiler and his associates (23) in nitrogen-hydrocarbon systems, which, unfortunately, are not of very great interest to aeronomy. It will be important to receive data on atmospheric reactions using ion cyclotron resonance in the future, both for what it can add in the way of new information and for

what it will contribute to understanding of present afterglow data.

2. Thermal to Medium Energies.

a. Secondary Ions in Mass Spectrometer Sources. This method needs little discussion here, having been treated in Ref. 1. However an important new advance has been applied to this approach by the use of photoionization sources for the primary ions. By using light of a given wave length, the primary ions can be much more selectively produced than on electron impact and production of ions in specific initial states is possible. Warneck (16) has been foremost in applying this important modification of an older method to problems of aeronomical interest.

b. Pulsed Sources on Mass Spectrometers. See Ref. 1.

c. Drift Tube Methods. In drift tube methods, primary ions are created at one end of a tube along the length which a dc electric field exists. A primary ion assumes a velocity appropriate to its mobility at the gas pressure in the tube and for the applied electric field. One effectively increases the kinetic temperature of the interactants without appreciably altering the internal energy states populations. A mass spectrometer usually samples the ions emerging from the drift tube which contains a buffer gas and the reactant gas of interest.

Three recent drift tube experiments are noteworthy. In the first, Hasted and his associates (15 and 24) changed the primary

ion source to be one which is mass analyzed and could be made state selective as well. Although the ion enters at relatively high energy (tens to hundreds of ev) it is rapidly moderated down in energy to the steady drift value. By inserting a selected ion into the drift tube, many of the ambiguities of interpretation of results are reduced.

Using groundstate O^+ ions reacting with N_2 to produce NO^+ an energy dependence of the rate coefficient which increased with energy was found, the increase being compatible with the increase in cross section for this reaction as obtained from crossed beam (25) and beam-in-static-gas (26) experiments. The apparent increase in rate coefficient for $O^+ + O_2 \rightarrow O + O_2^+$ at energies greater than 0.5 ev has already been noted earlier in this paper.

A second drift tube experiment of interest was the careful study of Heimerl, Johnsen and Biondi (27) on reactions between He^+ and both N_2 and O_2 , who showed that over the temperature range 300°K to 1200°K the reaction rate coefficients appear to be temperature-independent.

Yet a third drift tube experiment of interest is that of Golden, Sinnott and Varney (28) who studied the reaction $N_2^+ + O_2 \rightarrow N_2 + O_2^+$ and found that it also appeared to have a temperature-independent rate coefficient in accordance with the Langevin orbiting complex model.

d. Merging Beam Techniques. The newest experimental methods to arrive on the experimental scene is also one of the most elegant and promises to be extremely useful. This is the technique of merging parallel beams. In this method a fast beam of selected ions of mass m_1 at laboratory energy E_1 is charge-transfer neutralized and into this fast beam is merged a beam of ions of mass m_2 travelling at laboratory energy E_2 . After the two merged beams have run along together a prescribed distance (i.e., time) the ions are separated out and from the relative signals of the primary and secondary ions the cross section as a function of relative energy, or energy in the center of mass system, may be deduced.

The relative energy is given by

$$[14] \quad E_r = \frac{1}{m_1 + m_2} [\sqrt{m_2 E_1} - \sqrt{m_1 E_2}]^2$$

It is clear that even though the laboratory energies of the beams are quite high (high enough to produce and handle high current beams), by adjusting E_1 and E_2 the relative energy can be made arbitrarily small. Furthermore the energy spread in the center of mass is scaled down from the laboratory energy spread by a factor comparable to the relative energy divided by the laboratory energy. In this approach it is not necessary to be content to measure only rate coefficients, but instead cross sections as a function of energy as measured on

a very fine energy spread scale can be obtained.

This method which was first described by Trujillo, Neynaber, Marino and Rothe (29) has subsequently been applied by those authors to the charge transfer between $\text{Ar}^+ + \text{Ar}$. Of more interest for aeronomy, and also as an illustration of the unique potentialities of the merging beams technique, we can cite the very recent experiments of Entemann and Rol working in Dr. Neynaber's lab who examined collisions between O_2^+ and Na (private communication, 1968). Analysis of the secondary ions revealed the appearance of NaO^+ which was unequivocally identified, and the cross section for its formation corresponded to a thermal energy rate coefficient of approximately $8 \times 10^{-11} \text{ cm}^3/\text{sec}$. This product was also sought in the flowing afterglow experiments of Farragher et al (18) but without success due to general noise in the experiment.

While merging beam experiments are difficult to execute because of extremely low signal levels, they are extremely clean experiments and have very few interpretational pitfalls. The beams can be produced cleanly and impurity and competing process effects are automatically excluded; the product ions are unequivocally identified and there is no possibility of confusing different ions of the same e/m (e.g., H_5O_2^+ vs. NaN^+ , K^+ vs. NaO^+ , CO^+ vs. N_2^+ , etc.) which can occur in afterglow and drift tube experiments.

The merging beam technique appears to this author to be uniquely able to investigate reactions having small rate coefficients. While flowing afterglows appear suitable for determining large rate coefficients, when small rate coefficients are of interest, one must be extremely cautious in the flowing afterglow because of competing processes, perhaps with unknown impurities, to produce the desired secondary ion, attack of the secondary ion through tertiary processes, etc. Concerns of this kind probably need be worried about only for processes with apparent rate coefficients of 10^{-11} cm³/sec and less.

The one present problem with merging beams for ion-neutral studies of total cross sections is that the neutrals are produced by charge transfer and one is not certain of the internal energy state population of the neutral beam. Unquestionably, techniques will be developed to select states, perhaps such as that described in the following section, and correct this present deficiency.

3. Medium to High Energies.

At energies of a few ev and higher it is possible to produce ion beams of sufficiently high current to perform either beam-in-static-gas experiments or crossed beam experiments where the ion beam intersects a thermal energy molecular to atomic beam. Such experiments have been discussed in Refs. 1 and 2.

Recent work along these lines has continued with a wide variety of processes being examined. The rocket observations of Narcisi (4) have prompted crossed beam experiments on reactions producing and destroying metal ions. Henderson, Mentall and Fite (30) examined charge transfer between atmospheric ions and sodium and Turner and Rutherford (private communication, 1968) have made measurements on production of Mg^+ , Ca^+ , as well as Na^+ in charge transfer reactions between the parent metal atoms and N_2^+ , O_2^+ , N^+ , O^+ , NO^+ , H_2O^+ , and H_3O^+ to supplement a wide variety of measurements on atmospheric reactions between normally gaseous components (31).

Potentially the most important of the recent studies at the higher energies are those of Turner, Rutherford and Compton (32) on selective absorption of ions in beams passing through gases, for these point the way toward production of high currents of ions in specific states. A problem that has always plagued high energy experiments (and probably low energy experiments as well) is that it is difficult to produce ions in a single state and to know the state population in any ion beam. While one can produce the ions by electron bombardment immediately above threshold and gain reasonable assurance for most ions that only the groundstate ion is being produced, the ion currents so produced are often impossibly low. Turner and his associates took the approach to produce ions in an

electron bombardment source at high electron energies where the beam current was high, and then passed the current through an absorbing gas. Those ions in states with high cross sections for charge transfer or ion-molecule reactions will interact with the absorbing gas and be greatly attenuated, while those with low cross sections will be largely transmitted. Experimenting with O^+ and O_2^+ passing through N_2 , Ar and H_2 and looking at the transmitted current as a function of absorbing gas pressure, it was found that two clearly defined straight line sections on a semi-log plot appeared, demonstrating the existence of at least two separate cross sections for reaction for the ions in the beam. By reducing the electron energy to just above threshold, a single straight line appeared on the semi-log plot which was associated with the groundstate ion cross section. Comparing the semi-log plots, one can deduce (a) the fraction of ions in the beam which are excited when using the high electron energies (b) the cross section for the excited states reacting with the absorbing gas and (c) the cross section for the ground state reaction with the absorber. Among other things, it was learned that electron bombardment at energies typically used in ion sources produce 22 to 33% of the O_2^+ ions in the metastable $^4\Pi_u$ state and 27 to 30% of the O^+ appears to be in the 2D metastable state.

The cross sections are sufficiently different in these cases that with an absorber gas, the excited states can be virtually

completely removed while attenuating the groundstate ion component by a factor of only about 3 to 5. This can give an appreciable improvement in ion currents over sources operating immediately above threshold in order to produce the groundstate ion.

The potentialities of using selective attenuation to produce beams of ions in a given excited state are obvious and further experiments with different absorbing gases along these lines is clearly called for.

Of direct interest to aeronomy is the fact that the cross sections for reaction of the various states of O_2^+ colliding with N_2 at ion energies of about 100 ev differ by factors of 150! Whether many thermal reaction rates also have such spectacular variation with the state of the ionic reactant will be something very important to learn, especially for application to aeronomic situations where ions in excited states can be produced.

It is this author's expectation that a review paper on the subject of reactions between positive ions and neutral molecules given five years hence will have as its central theme the role of excited states.

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TABLE OF RATE COEFFICIENTS AT 300°K

(Where several measurements exist \pm indicates approximate range of measured values; where single measurements exist \pm indicates estimated experimental uncertainty. Notation "A(-B)" implies $A \times 10^{-B}$. Extrapolated values from High Energy data are not included in this table.)

Reaction	k (cm ³ /sec)	References and Comments
$\text{He}^+ + \text{O}_2 \rightarrow \text{He} + \text{O} + \text{O}^+$	10 ± 5 (-10)	1-7
$\text{He}^+ + \text{N}_2 \rightarrow \text{He} + \text{N} + \text{N}^+$	12 ± 5 (-10) total	2-i
$\text{He}^+ + \text{N}_2 \rightarrow \text{He} + \text{N}_2^+$	Branching: $\text{N}^+ \sim 65\%$ $\text{N}_2^+ \sim 35\%$	
$\text{O}^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{N}$	2 ± 1 (-12)	5, 7, 9, 10, 11, 12, 18, 19 Importance of vibrational temperature in N_2 established by Schmeltekopf et al, Ref. 13
$\text{O}^+ + \text{O}_2 \rightarrow \text{O} + \text{O}_2^+$	2 ± 1 (-11)	7, 9, 10, 11, 12, 14
$\text{N}_2^+ + \text{O}_2 \rightarrow \text{N}_2 + \text{O}_2^+$	$1 \pm .5$ (-10)	1, 3, 5, 7, 9, 15
$\text{N}_2^+ + \text{O} \rightarrow \text{NO}^+ + \text{N}$	2.5 (-10)	16
$\text{N}_2^+ + \text{O} \rightarrow \text{N}_2 + \text{O}^+$	< 1 (-11)	16
$\text{O}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{O}_2$	8 (-10)	7, 17
$\text{O}_2^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{NO}$	< 1 (-15)	7, 17
$\text{O}_2^+ + \text{N} \rightarrow \text{NO}^+ + \text{O}$	$18.$ (-10)	17
$\text{N}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{N}_2$	5 (-10)	7, 17
$\text{N}^+ + \text{O}_2 \rightarrow \text{NO}^+ + \text{O}$	3.5 ± 1.5 (-10)	1, 5, 7, 9, 17
$\text{N}^+ + \text{O}_2 \rightarrow \text{N} + \text{O}_2^+$	4.5 ± 1.5 (-10)	5, 7, 9, 17
$\text{N}_2^+ + \text{Na} \rightarrow \text{N}_2 + \text{Na}^+$	5.8 ± 3.8 (-10)	20
$\text{O}_2^+ + \text{Na} \rightarrow \text{O}_2 + \text{Na}^+$	6.7 ± 2.1 (-10)	20
$\text{O}_2^+ + \text{Na} \rightarrow \text{NaO}^+ + \text{O}$	7.7 ± 2.4 (-11)	21 (Merging beam Result)

Reaction	k (cm ³ /sec)	References and Comments
$\text{NO}^+ + \text{Na} \rightarrow \text{NO} + \text{Na}^+$	7 ± 2 (-11)	20
$\text{Mg}^+ + \text{O}_3 \rightarrow \text{MgO}^+ + \text{O}_2$	2.3 (-10)	22
$\text{MgO}^+ + \text{O} \rightarrow \text{Mg}^+ + \text{O}_2$	~ 1 (-10)	24
$\text{Ca}^+ + \text{O}_3 \rightarrow \text{CaO}^+ + \text{O}_2$	1.6 (-10)	22
$\text{Fe}^+ + \text{O}_3 \rightarrow \text{FeO}^+ + \text{O}_2$	1.5 (-10)	22
$\text{Na}^+ + \text{O}_3 \rightarrow \text{NaO}^+ + \text{O}_2$	< 1 (-11)	22
$\text{NO}^+ + \text{O}_3 \rightarrow \text{NO}_2^+ + \text{O}_2$		very slow, unobservable in flowing afterglow
$\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}$	8,5 (-10)	25
$\text{H}_2\text{O}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{H}_2\text{O}$	~ 2 (-10)	26
$\text{O}^+ + \text{CO}_2 \rightarrow \text{O}_2^+ + \text{CO}$	1.2 (-9)	27
$\text{N}^+ + \text{CO}_2 \rightarrow \text{CO}_2^+ + \text{N}$	1.3 (-9)	28
$\text{N}_2^+ + \text{CO}_2 \rightarrow \text{CO}_2^+ + \text{N}_2$	9 (-10)	28
$\text{N}^+ + \text{CO} \rightarrow \text{CO}^+ + \text{N}$	5 (-10)	28
$\text{N}_2^+ + \text{CO} \rightarrow \text{CO}^+ + \text{N}_2$	7 (-11)	28
$\text{C}^+ + \text{O}_2 \rightarrow \text{CO}^+ + \text{O}$	1.0 ± 1.1 (-9)	29, 30
$\text{C}^+ + \text{CO}_2 \rightarrow \text{CO}^+ + \text{CO}$	1.9 (-9)	29
$\text{CO}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{CO}$	2.0 (-10)	29
$\text{CO}^+ + \text{CO}_2 \rightarrow \text{CO}_2^+ + \text{CO}$	1.1 (-9)	29
$\text{CO}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{CO}_2$	1.0 (-10)	31

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